ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 146 (2002) 149–155

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Comparison of methods for the photochemical degradation of chlorophenols

T. Pandiyan [a,*], O. Martínez Rivas [a], J. Orozco Martínez [a],
G. Burillo Amezcua [b], M.A. Martínez-Carrillo [a]

[a] *Facultad de Quìmica, Universidad Nacional Autónoma de México (UNAM), México 04510, México*
[b] *Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México (UNAM), México 04510, México*

Received 1 October 2001; accepted 6 October 2001

Abstract

Mono/polychlorophenols are currently used for a wide range of domestic, agricultural and industrial purposes. The improper disposal of mono/polychlorophenols in landfills and in low-temperature combustion contributes significantly to environmental contamination. Generally, chlorinated aromatic phenols are toxic to living organisms. For example, pentachlorophenol can affect sensitive organisms, even at low concentrations and lead to alterations in ecosystems. The objective of the present study is to investigate dehalogenation and destruction of halogenated phenols by using photochemical methods. The reactants and products were analyzed by gas chromatography. Dehalogenation was faster for monohalogenated phenols than poly-substituted phenols. Experimental data demonstrate that the reaction rate of dehalogenation in the presence of TiO_2 is 4-chlorophenol > 2,4,-dichlorophenol > 2,4,6-trichlorophenol. To overcome the low solubility of higher chlorinated phenols in aqueous systems, the mixture of water/methanol (60:40) was used; however, the methanolic mixture affects photodegradation rates of the chlorophenols.

Keywords: 4-Chlorophenol; 2,4-Dichlorophenol; 2,4,6-Trichlorophenol; TiO_2; Photochemical reaction

1. Introduction

Organic pollutants include alkanes, haloalkanes, aliphatic alcohols, carboxylic acids, alkenes, polymers, surfactants, herbicides, pesticides and dyes as well as aromatic and haloaromatics which are commonly present in industrial wastewater. Monochlorophenols are mainly used as intermediates in dyestuffs and in the manufacture of higher chlorinated phenols; 2,4-dichlorophenol (DCP) is used in larger volumes in the manufacture of 2,4-dichlorophenoxyacetic acid. An important isomer in the trichlorophenol series is 2,4,5-trichlorophenol and is used as an intermediate in the manufacture of the herbicide 2,4,5-trichlorophenoxyacetic acid. The 2,3,4,6-tetrachlorophenol is available commercially and is used as a preservative. Pentachlorophenol and its sodium salt are used extensively as antimicrobial agents and have a broad spectrum of pesticidal efficacy. The improper disposal of mono/polychlorophenols in landfills and in low-temperature combustion contributes significantly to environmental contamination. Although the chlorinated aromatic phenols generally are toxic to living organisms, pentachlorophenol is more toxic to plants, animals and humans [1]. Pentachlorophenol can affect sensitive organisms, even at low concentrations of 0.1–1.0 μg/l and lead to alterations in the ecosystems.

In recent years, advanced oxidation processes (AOP) emerged as potentially powerful methods for transforming pollutants into harmless substances [2]. An AOP which has a considerable success is photolytic oxidation by UV light combined with strong oxidants such as hydrogen peroxide and perchlorate [3]. It has been proved that this process can completely destroy many toxic organic compounds in wastewater into carbon dioxide [4–6]. The overall process can be summarized by the following reaction:

$$\text{Organic pollutants} + O_2 \rightarrow CO_2 + H_2O + \text{mineral acid}$$

The photochemical treatment of mono/polychlorophenol is now at commercial stage of development [7]. Generally, degradation is slower for higher chlorinated phenols, such as pentachlorophenol, or those with a chlorine atom in the *meta* position [8]. There is concern that highly toxic products, such as polychlorinated dibenzo-*p*-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs) are generated during the UV treatment of polychlorophenol [9–11]. Earlier studies [11] indicate that PCDDS and PCDFs are

---

[*] Corresponding author. Fax: +52-5-6223712.
E-mail address: pandiyan@servidor.unam.mx (T. Pandiyan).

1010-6030/02/$ – see front matter

PII: S1010-6030(01)00606-2

formed as intermediates when pentachlorophenol is treated with a low-pressure mercury lamp (6 W emitting at 254 nm). These compounds are certainly more harmful than pentachlorophenol itself. In order to avoid these potential toxic intermediates, other studies have proposed the combination of UV irradiation and oxidizing agents, such as ozone, H_2O_2 or photocatalysts, such as TiO_2 [12–15].

It has been well demonstrated that when TiO_2 is illuminated by light ($\lambda < 380$ nm) in presence of water containing dissolved oxygen and organic compounds, photodegradation of the organic compounds will occur. The primary step in the photodegradation is the generation of electrons and valence band holes within the TiO_2 particles.

$$\mathrm{TiO_2} \rightarrow \mathrm{TiO_2(e^- + h^+)}$$

In the presence of dissolved oxygen and an electron donor, $OH^\bullet$ radical is formed by the reaction between the valance band holes (h^+) and the TiO_2 surface active $OH^\bullet$ group or H_2O.

$$h^+ + \mathrm{OH^-} \rightarrow \mathrm{OH^\bullet}$$

$$h^+ + \mathrm{H_2O} \rightarrow \mathrm{OH^\bullet} + \mathrm{H^+}$$

The photogenerated holes and electrons react with surface adsorbed species producing $OH^\bullet$ radicals and superoxide ions [16]. The hydroxyl radical is a strong oxidizing agent and highly reactive and is believed to be responsible for degradation of organic molecules. The objective of the present study is to investigate dehalogenation and destruction of halogenated phenols by using photochemical methods and also to compare the photochemical rate of reactions of mono/polychlorophenols. To distinguish the role of catalyst and oxidants in the photocatalytic degradation process in phenolic compounds, three kinds of methods are used: (1) direct UV irradiation; (2) UV irradiation in presence of TiO_2 and (3) UV light with TiO_2 (catalyst) and $ClO_4{}^-$ (oxidants). The possibility of increasing the rates of photodegradation of chlorinated hydrocarbons by using UV/TiO_2 with inorganic oxidants such as $IO_4{}^-$ and $BrO_3{}^-$ is under investigation.

2. Materials and methods

2.1. Materials

The following chemicals were used as received: 4-chlorophenol (CP), DCP and 2,4,6-trichlorophenol (TCP) (Aldrich); titanium dioxide (Prolabo Germany); sodium perchlorate and methanol (Merck).

2.2. Instruments

The following instruments were used in the experimental protocol. The schematic experimental details of photocatalytic reactor is shown in Fig. 1. A 100 W immersion UV lamp equipped with a quartz well and voltage regulator (Ace Glass, USA) was employed for UV degradation. Gas chromatography (GC-9000, Perkin-Elmer) using a capillary column and flame ionization detector (FID) was used to quantify the parent mono/polychlorophenols. UV–VIS spectroscopy (Perkin-Elmer, Lambda 2) was used to measure the absorbance of chlorophenols in presence of perchlorate ions.

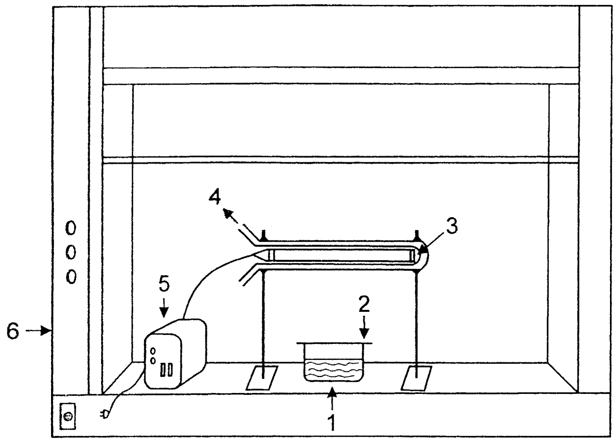


Fig. 1. Schematic diagram of photochemical experiment: (1) chlorinated phenolic compounds in quartz beaker; (2) quartz plate; (3) UV lamp in quartz jacket; (4) water circulation; (5) voltage regulator; (6) chamber.

3. Experiments

3.1. UV irradiation of polychlorophenols

To understand the respective importance of oxidant and photocatalyst, we evaluated three methods to treat the phenolic compounds, represented by the following equations:

$$\text{Phenolic compounds} \xrightarrow{\text{UV irradiation}} \text{degraded products} \quad \text{(method 1)}$$

$$\text{Phenolic compound} \xrightarrow{\text{UV/TiO}_2} \text{degraded products} \quad \text{(method 2)}$$

$$\text{Phenolic compounds} + \text{oxidant} \xrightarrow{\text{UV/TiO}_2} \text{degraded products} \quad \text{(method 3)}$$

In the first method, the chlorophenolic compounds (20 ml, 1 mM) in methanol/water (40:60) solution were treated with direct UV irradiation at 25 °C. During the UV irradiation, chlorophenols were analyzed at 30 m intervals. The solutions were filtered through a 0.45 μm nylon filter unit before GC analysis. The GC column temperature was 85 °C for CP and DCP compounds; the column temperature was elevated to 115 °C for TCP to avoid deposition of compound crystals in the column. Chromatographic analysis was performed in triplicate.

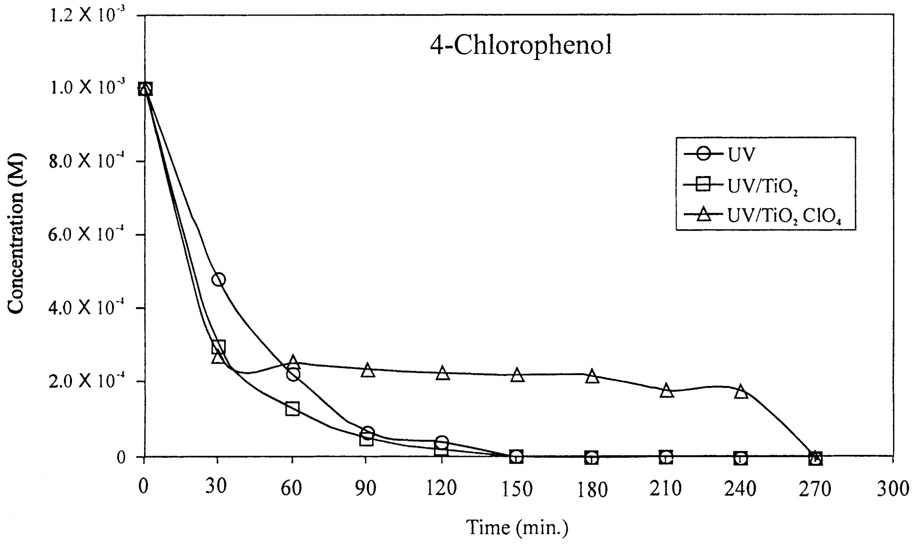


Fig. 2. Plot of concentration vs. time for CP during the photochemical irradiations. The rate constants: $k = 2.69 \times 10^{-2}$ for direct UV irradiation; $k = 3.52 \times 10^{-2}$ for UV/TiO_2.

In the second method, the solutions were irradiated with UV light in presence of photocatalyst, TiO_2 (4 g/l). The photocatalyst was added after the measuring the initial concentration (1.0 mM) of chlorophenols. Other experimental procedures were the same as described in the first method. Finally, the solutions were treated with UV light in presence of photocatalyst (TiO_2) and also with oxidant (ClO_4^-, 0.03 M). Because perchlorate ions affect the GC column, UV–VIS spectroscopy was used to quantify the chlorophenols at 30 m intervals. The pH was measured before and after UV irradiation.

4. Results and discussion

4.1. Degradation of polychlorophenols

The experimental data depicted in Fig. 2 indicates that CP using UV light alone degrades considerably with time. Though the initial concentration (1.0×10^{-3} M) of CP was reduced to 3.8×10^{-5} M within 120 min by direct UV irradiation, the decrease is faster in presence of photocatalyst (TiO_2). The first-order reaction rate constants ($k = 2.69 \times 10^{-2}$ for direct UV irradiation; $k = 3.52 \times 10^{-2}$ for

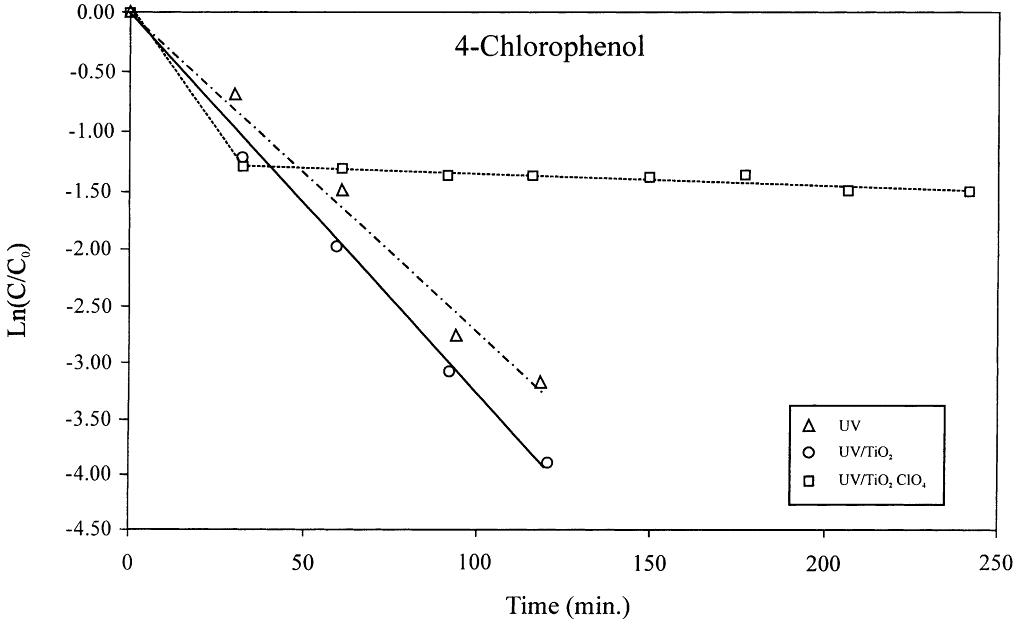


Fig. 3. Ln(C/C_0) vs. time of CP.

UV/TiO_2) indicate TiO_2 accelerates the rate of reaction. A plot Ln(C/C_0) against time of CP is shown in Fig. 3 and indicates that photo-oxidation of CP on TiO_2 follows first-order kinetics. However, in the case of the photocatalytic reaction in presence of perchlorate, we did not obtain expected results. Though the rate of reaction was higher in the initial 30 min when compared to the non-perchlorate treatments (Fig. 2), the rate decreased significantly in the remaining reaction period (40–240 min). The initial rapid rate is likely due to adsorption of phenolic compounds which facilitates degradation. After the 40 min, there is a possibility of saturation of chlorinated phenol on the catalyst. The experimental data indicates the TCP reaction is faster than other compounds (TCP > DCP > CP) in the initial stage of the reaction. This is likely due to the fact that highly substituted phenols are strongly adsorbed on the catalyst [17]; specifically, the adsorption of higher chlorinated phenolic compounds on the surface of catalyst is greater than the less chlorinated compounds, which accelerates the degradation reaction. However, after the 40 min, saturation of the adsorption sites occurs on the surface of the catalyst. The higher deposition of chlorides from chlorinated compounds (or from the perchlorates) on the surface of TiO_2 could change the pH and hinder further reaction. Previous work by Lu et al. [18] indicates that at both low and high pH values photodegradation rates are quite slow. There is also possibility that evolution of O_2 molecules from $NaClO_4$ reduces the rate of reaction. However, it is premature to predict these behaviors and we need further study on these reactions.

The chromatographic data show that the chlorophenol peak height decreases during the photochemical reaction while a new signal was detected at 2.15 min retention time. This signal grew at the expense of the reduction of CP peak (Fig. 4) and matches the GC retention time of phenol. However, earlier studies [19,20] indicate that the 4-chlorodihydroxycyclodienyl radical is first formed, then converts to hydroquinone. Further investigation to characterize this product using IR spectroscopy indicates the presence of a C=O group. Further investigation is needed to determine if this product is hydroquinine or association of phenolic with hydroquinine. A possible mechanism for the products by both reductive (Scheme 1) and oxidative (Scheme 2) pathways are given below.

The pH value of the irradiated solution decreased from 6.5 to 3.35 (direct UV irradiation), 6.5 to 2.70 (UV/TiO_2), and 6.5 to 2.55 (UV/TiO_2/ClO_4). pH is an important parameter in photodegradation on the surface of TiO_2-photocatalyst. The point of zero charge (PZC) for TiO_2 is between pH 5.6 and 6.4 [18,21]. Hence, at more acidic pH values, the catalyst surface is positively charged and will have a significant effect on the adsorption/desorption properties at the catalyst surface. At low values photodegradation rates are quite slow. The best pH value for degradation is near the PZC of TiO_2 [18–21].

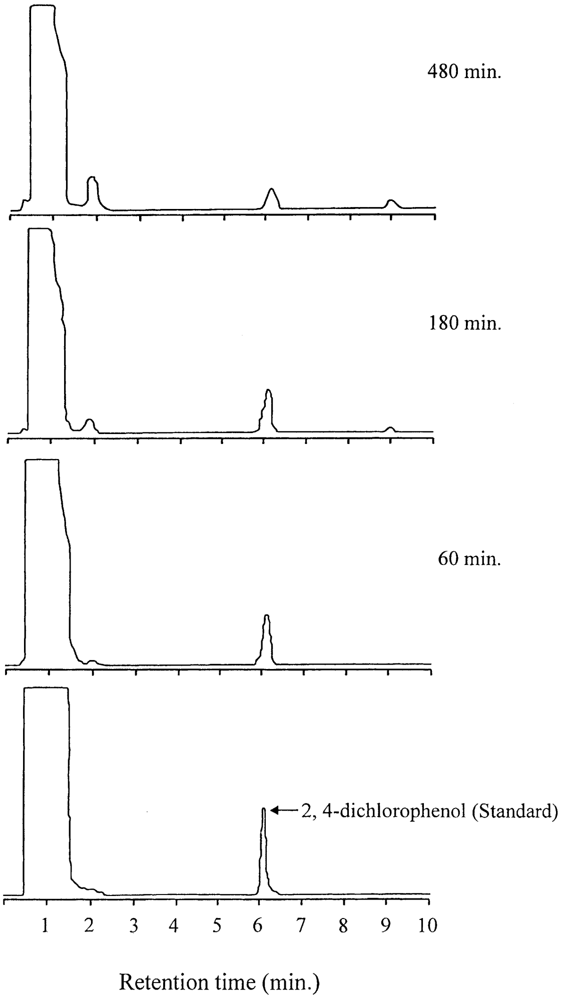
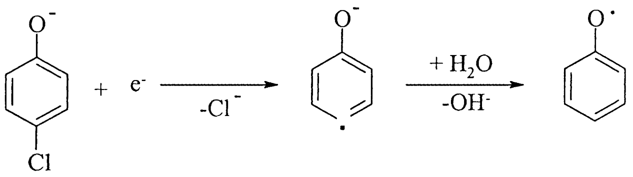
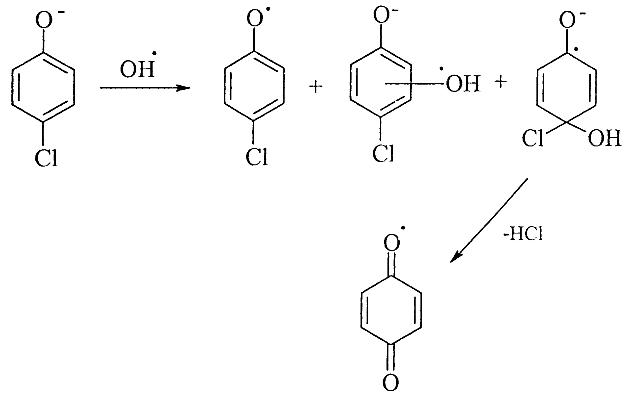


Fig. 4. Gas chromatograms of CP during the UV irradiation in presence of TiO_2.

In the case of DCP, graphical analysis of the photochemical data (Fig. 5) shows that the initial concentration of DCP (1.0×10^{-3} M) was gradually reduced to 2.00×10^{-4} M in 480 min by using direct UV irradiation. Photocatalytic degradation of DCP was accelerated in the presence of TiO_2 catalyst as indicated by the first-order rate constants ($k = 2.58 \times 10^{-3}$ for direct UV irradiation; $k = 3.87 \times 10^{-3}$ for UV/TiO_2). A plot of Ln(C/C_0) against time is shown in Fig. 6. It is interesting to note that the behavior of the degradation process in presence of oxidant is the same as observed in CP. Initially, degradation of the compound is rapid then steadily declines. The reaction rates (Figs. 5 and 6) in decreasing order are UV/TiO_2/ClO_4 > UV/TiO_2 >



Scheme 1. Electron attachment onto the CP anion and the production of the phenoxy radical.



Scheme 2. Reaction between the hydroxyl radical and the CP anion yielding hydroquinone anion.

$\mathrm{ClO_4}$ before the 90 min and UV/$\mathrm{TiO_2}$ > UV/$\mathrm{TiO_2}$/$\mathrm{ClO_4}$ > UV after the 90 min. The decrease in the peak intensities of DCP was concomitant with a increase in new signals at RT of 8.9 and 2.15 that corresponds to CP and phenol standards. This result is similar to that observed for CP. Earlier reports do not indicate phenol as an intermediate during the process of dechlorination of chlorinated phenol. Further investigation is needed to isolate these compounds.

In the case of TCP, the rate constants calculated from the experimental data are 1.99×10^{-3} for direct UV irradiation and 3.34×10^{-3} for UV/$\mathrm{TiO_2}$. TCP concentrations versus time are shown in the Fig. 7 and $\mathrm{Ln}C/C_0$ values versus time are presented in Fig. 8. Chromatographic analysis showed reaction products at RT of 2.30, 2.65 and 4.45 min which correspond to phenol dichlorophenol and chlorophenol.

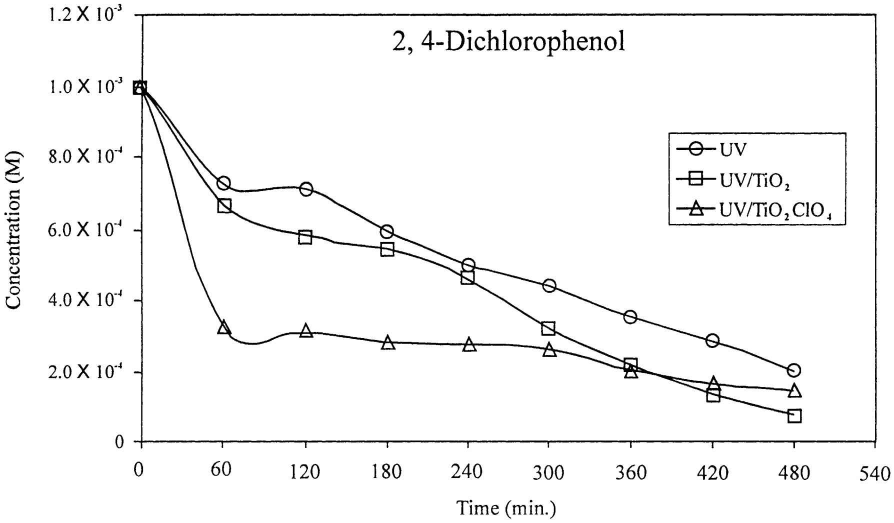


Fig. 5. Photochemical irradiation process of DCP with time. The rate constants: $k = 2.58 \times 10^{-3}$ for direct UV irradiation; $k = 3.87 \times 10^{-3}$ for UV/$\mathrm{TiO_2}$.

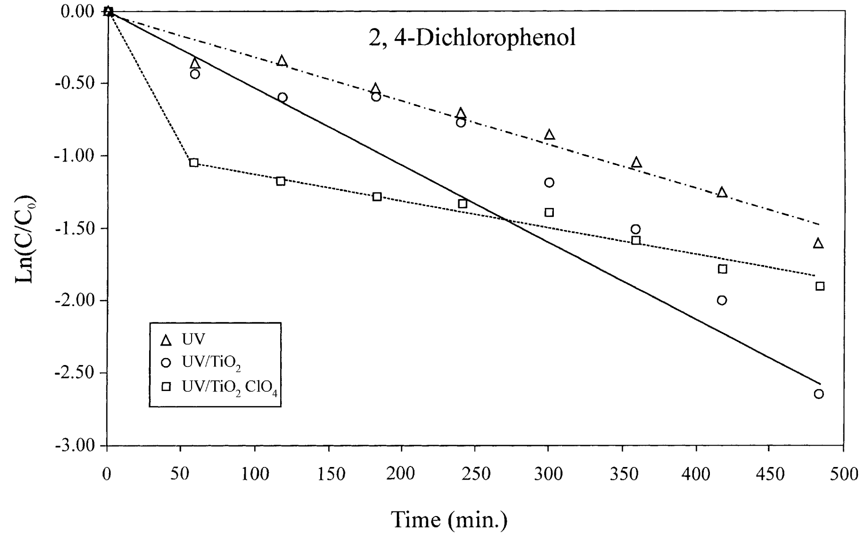


Fig. 6. $\mathrm{Ln}(C/C_0)$ vs. time of DCP.

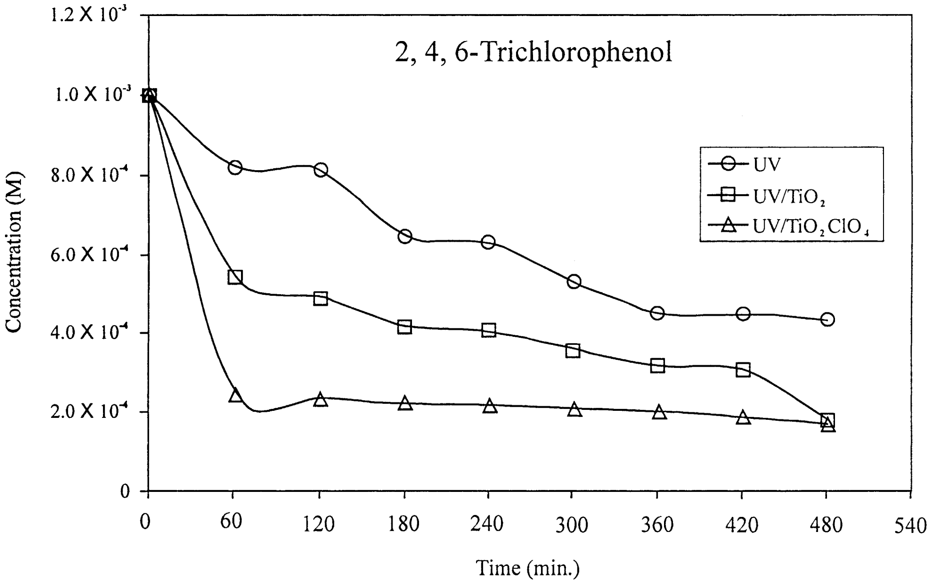


Fig. 7. Concentration against time during the photochemical irradiation of TCP. The rate of reactions are $k = 1.99 \times 10^{-3}$ for direct UV irradiation; $k = 3.34 \times 10^{-3}$ for UV/TiO_2.

Jardim et al. [22] studied the photodegradation of chlorophenols using aqueous suspension of TiO_2 as a catalyst and the observed first-order rate constant was $k = 0.0328\,\mathrm{min}^{-1}$ for DCP. However, our experimental results indicate that corresponding rate constant was reduced to $0.00387\,\mathrm{min}^{-1}$ in the water/methanol mixture used in this study 10 times. A somewhat higher rate was observed for TCP ($k = 0.0054\,\mathrm{min}^{-1}$) in water system of compound to the rate observed in methanolic/water system ($k = 0.0034$). Adsorption and pH are more important factors in the photochemical chlorinated phenol. In addition, the solvents also have a impact on rate of degradation of chlorophenols. This is likely fact that a possibility to generate $OH^{\bullet}$ radical in protic solvent like water is much higher and consequently increases the rate of the degradation of DCP; furthermore, a higher solubility of dissolved oxygen in water than methanol/water system also helps the photochemical reaction rate. In the previous study, the amount of chlorophenols removed due to TiO_2 (mmol/g) adsorption were 0.063 (CP); 0.028 (DCP); 0.077 (TCP) was established; indicating that

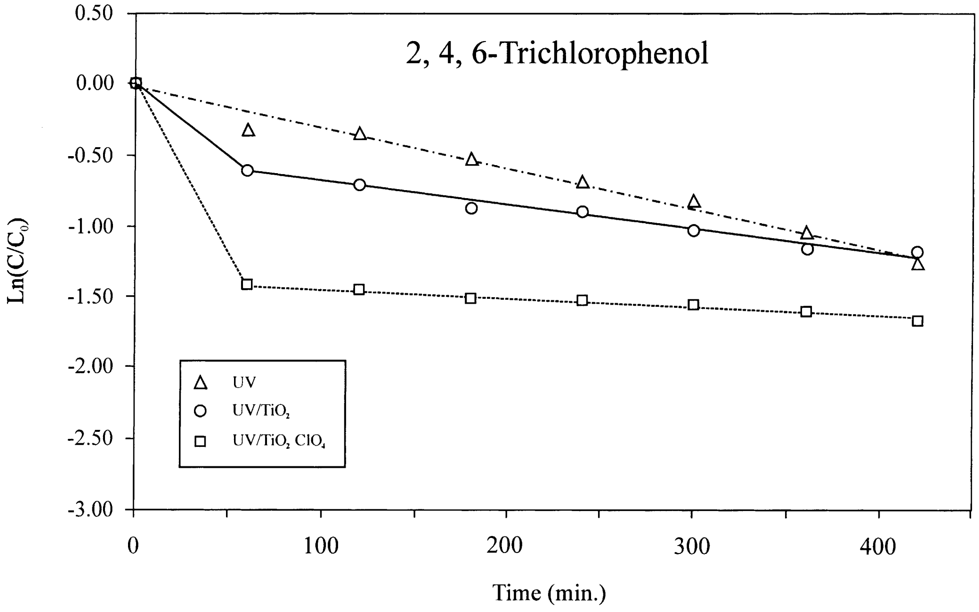


Fig. 8. Ln(C/C_0) vs. time of TCP.

the amount of TCP adsorption by TiO_2 is largest among these compounds [23,24]; this is consistent with the higher rate constant observed for TCP.

5. Conclusions

Photocatalytic oxidation of chlorinated phenols is facilitated by presence of catalyst or catalyst combined with oxidant. The presence of perchlorate as oxygen source, initially it helps to accelerate the reaction, however, it slow down the reaction after 40 min, it may be due to higher deposition of chloride ions or saturation of adsorption of chlorinated compounds on the surface of TiO_2. Depending upon the degree of dechlorination, the decomposition rate decreases in the order: CP $>$ DCP $>$ TCP.

Acknowledgements

The authors acknowledge the Consejo Nacional de Ciencia y Tecnologia (Project No. 32759-N) and Dirección General de Asuntos del Personal Académico Personal (DGAPA IN 205398) for their economic support. We also thank Unidad de Servicios de Apoyo e Investigación USAI, UNAM for providing spectral facilities, and also thank E. Bucio for technical support.

References

[1] E.D. Packham, C.L. Duxbury, C.I. Mayfield, W.E. Inniss, J. Kruuv, J.E. Thompson, Contam. Bull. Environ. Toxicol. 29 (1982) 739.
[2] Y.S. Shen, Y. Ku, Ind. Pollut. Prevent. Control 56 (1995) 278.
[3] J. Staehelin, J. Hoigne, Environ. Sci. Technol. 19 (1985) 1206.
[4] D.F. Ollis, E. Pelizzetti, N. Serpone, Heterogeneous photocatalysis in the Environment: application to water purification, in: N. Serpone, E. Pelizzetti (Eds.), Photocatalysis: Fundamentals and Applications, Wiley/Interscience, New York, 1989, pp. 603–637.
[5] J.C. D'Oliverira, G. Al-Sayyed, P. Pichat, Environ. Sci. Technol. 24 (1990) 990.
[6] K. Okamoto, Y. Yamamoto, H. Tanaka, A. Itaya, Bull. Chem. Soc. Jpn. 58 (1985) 2023.
[7] J.R. Bolton, S.R. Cater, Homogeneous photodegradation of pollutants in contaminated water: an introduction, in: R.G. Zepp, G.R. Helz, D.G. Crosby (Eds.), Aquatic and Surface Photochemistry, Lewis Publishers, Boca Raton, FL, 1994, pp. 467–690.
[8] N. Getoff, S. Solar, Radiat. Phys. Chem. 28 (1986) 443.
[9] A.S. Wong, D.G. Crosby, Photolysis of pentachlorophenol in water, in: K.R. Rao (Ed.), Pentachlorophenol, Chemistry, Pharmacology, and Environmental Toxicology, Plenum Press, New York, 1978, pp. 19–25.
[10] G.G. Choudhry, O. Hutzinger, Photochemical formation and degradation of polychlorinated dibenzofurans and dibenzo-*p*-dioxins, in: F.A. Gunther (Ed.), Residue Reviews, Vol. 84, Springer, New York, 1982, pp. 133–160.
[11] S. Vollmuth, A. Zajc, R. Niessner, Environ. Sci. Technol. 28 (1994) 1145.
[12] G.G. Choudhry, G.R.B. Webster, Environmental aquatic photochemistry of polychlorophenols, in: M. Schiavello (Ed.), Photocatalysis and Environment, Trends and Applications, Vol. 237, NATO ASI Series C, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1988, pp. 691–692.
[13] E. Pelizzetti, E. Pramauro, C. Minero, N. Sepone, E. Borgarello, Photodegradation of organic pollutants in aquatic systems catalyzed by semiconductors, in: M. Schiavello (Ed.), Photocatalysis and Environment, Trends and Application, Vol. 237, NATO ASI Series C, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1998, pp. 469–497.
[14] E.R. Haag, C.C.D. Yao, Environ. Sci. Technol. 26 (1992) 1005.
[15] G. Mills, M.R. Hoffmann, Environ. Sci. Technol. 27 (1993) 1681.
[16] D. Chen, A.K. Ray, Water Res. 32 (1998) 3223.
[17] A.P. Davis, C.P. Huang, Water Res. 24 (1990) 543.
[18] M.C. Lu, G.D. Roam, J.N. Chen, C.P. Huang, J. Photochem. Photobiol. A: Chem. 76 (1993) 103.
[19] S.T. Martin, C.L. Morrison, M. R Hoffman, J. Phys. Chem. 98 (1994) 13695.
[20] J. Tseng, C.P. Huang, Photocatalytic Oxidation Process for the Treatment of Organic Wastes. Chemical Oxidation Technologies for the Nineties (Editorial), Vol. 1, Technomic Publishing Company, Pensilvania, USA, 1994, pp. 254–277.
[21] R. Terzian, N. Serpone, J. Photochem. Photobiol. A: Chem. 89 (1995) 163.
[22] W.F. Jardim, S.G. Moraes, M.M.K. Takiyama, Water Res. 7 (1997) 1728.
[23] J.N. Chen, Y.C. Chan, M.C. Lu, Water Sci. Tech. 39 (1999) 225.
[24] S. Tanaka, U.K. Saha, Water Sci. Tech. 30 (1994) 47.